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US-PAT-NO: 5096586

DOCUMENT-IDENTIFIER: US 5096586 A

TITLE: Membranes having selective permeability

DATE-ISSUED: March 17, 1992

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Kaher; Richard E.	Beverly Hills	CA		
Anderson; Mark E.	Los Angeles	CA		
Mattes; Benjamin R.	Los Angeles	CA		
Reiss; Howard	Encino	CA		

US-CL-CURRENT: 210/500.37; 264/41, 264/DIG.48, 264/DIG.62

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw. Desc	Image								

KMC

☐ 4. Document ID: US 5085775 A

L31: Entry 4 of 8

File: USPT

Feb 4, 1992

US-PAT-NO: 5085775

DOCUMENT-IDENTIFIER: US 5085775 A

TITLE: Thin film composite ultrafiltration membrane

DATE-ISSUED: February 4, 1992

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Swamikannu; A. Xavier	Mount Prospect	IL		

US-CL-CURRENT: 210/500.27; 210/500.34, 210/500.35, 210/500.41, 210/500.42, 210/506,
264/45.5, 427/245

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw. Desc	Image								

KMC

☐ 5. Document ID: US 4964998 A

L31: Entry 5 of 8

File: USPT

Oct 23, 1990

US-PAT-NO: 4964998

DOCUMENT-IDENTIFIER: US 4964998 A

TITLE: Use of treated composite polyamide membranes to separate concentrated solute

DATE-ISSUED: October 23, 1990

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cadotte; John E.	Minnetonka	MN		
Racchini; Joel-Raphael	St. Louis Park	MN		
Petersen; Robert J.	Minneapolis	MN		

US-CL-CURRENT: 210/654; 210/500.38

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Drawn Desc	Image								

KWC

☐ 6. Document ID: US 4960518 A

L31: Entry 6 of 8

File: USPT

Oct 2, 1990

US-PAT-NO: 4960518

DOCUMENT-IDENTIFIER: US 4960518 A

TITLE: Treatment of composite polyamide membranes with compatible oxidants

DATE-ISSUED: October 2, 1990

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cadotte; John E.	Minnetonka	MN		
Racchini; Joel R.	St. Louis Park	MN		

US-CL-CURRENT: 210/639; 210/500.38, 210/651, 210/652

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Drawn Desc	Image								

KWC

☐ 7. Document ID: US 4960517 A

L31: Entry 7 of 8

File: USPT

Oct 2, 1990

US-PAT-NO: 4960517

DOCUMENT-IDENTIFIER: US 4960517 A

TITLE: Treatment of composite polyamide membranes via substitution with amine reactive reagents

DATE-ISSUED: October 2, 1990

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cadotte; John E.	Minnetonka	MN		

US-CL-CURRENT: 210/639, 210/500.38, 210/651, 210/652

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Drawn Desc	Image								

KWC

Journal of Management Education 30(6)

DATE-ISSUED: May 16, 1989

INVENTOR- INFORMATION				
NAME	CITY	STATE	ZIP CODE	COUNTRY
Tran; Chinh N.	San Diego	CA		
Chu; Hong C.	San Diego	CA		
Light; William G.	San Diego	CA		

US-CL-CURRENT: 427/245; 210/500.33, 210/500.37, 210/500.38, 210/500.41, 427/341,
428/420

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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Entry 1 of 8

File: USPT

Oct 25, 1994

DOCUMENT-IDENTIFIER: US 5358556 A
 TITLE: Membranes having selective permeability

Brief Summary Paragraph Right (12):

U.S. Pat. No. 4,615,829 to Tamura et al. describes an electroconductive organic polymer containing an electron acceptor as a dopant and consisting essentially of a linear polymer having as a main repeating unit a quinoxalinediimine structure. According to Tamura et al., this polymer is prepared by oxidative or electro-oxidative polymerization of an aniline compound or a water-soluble salt thereof in a reaction medium containing a protonic acid. The product is a conductive polymer which exhibits stability without an additional doping step, because it allegedly has already undergone doping during the course of the oxidative polymerization. Tamura et al. suggests that the polymer may be chemically compensated with ammonia, whereby it undergoes significant loss of electroconductivity; if this polymer is then doped with an electron acceptor such as sulfuric acid, the original high electro-conductivity is restored. There is described a process wherein the polymer is produced by first reducing the electroconductive organic polymer with a reducing agent and then oxidizing and simultaneously doping the reduced polymer with an oxidizing agent which is effective as an electron acceptor, in this manner, the dopant may be replaced by a different dopant such as a halogen or Lewis acid. While no particular utility for the electroconductive polymers of Tamura et al. is disclosed, it is apparent from the specification that the salient feature of the subject materials is an electroconductivity of not less than 10 sup.-6 S/cm .

Detailed Description Paragraph Right (28):

Morphological changes that result in improved gas selectivities may be produced in conjugated base-type polymers (such as polyaniline) by exposure to either Bronsted or Lewis acids. The former induce protonic acid doping of the nitrogen atoms along the polymer backbone to form covalent N-H bonds. The most generalized formula for the Bronsted acids is H-X . X dissociates to form one of two species: an inorganic anion X sup.- , such as fluoride (F sup.-), chloride (Cl sup.-), bromide (Br sup.-), iodide (I sup.-), bisulfate (HSO sub.3 sup.-), nitrate (NO sub.3 sup.-), perchlorate (ClO sub.4 sup.-), etc.; or an organic anion X sup.- , such as trisylate ($\text{BrC sub.6 H sub.4 SO sub.3 sup.-}$), acetate ($\text{CH sub.3 CO sub.2 sup.-}$), formate (HCO sub.2 sup.-), etc. Selection of a suitable Bronsted acid on the basis of, e.g., the size of the anion desired for a given system would be well within the skill of those working in the field.

Detailed Description Paragraph Right (29):

Similar changes can be effected in the polymer films by reaction with acids that accept electron density (Lewis acids) from, e.g., the lone pair of the polyaniline nitrogen to form carbon-nitrogen, silicon-nitrogen, sulfur-nitrogen, oxygen-nitrogen, phosphorus-nitrogen, etc., coordinate covalent bonds during the doping process. These Lewis acid compounds may be represented as RX , R sub.3 OX , R sub.2 SO sub.2 , R' SO sub.2 Cl , etc., wherein R or R' is alkyl or alkenyl (for example, of 1 to 10 carbon atoms), or is aryl or aralkyl (e.g., tosyl, benzyl, tolyl, xylyl or other aromatic groups). X represents anionic species such as chloride (Cl sup.-), fluoride (F sup.-), iodide (I sup.-), bromide (Br sup.-), hexafluorophosphate (PF sub.6 sup.-), hexafluorophosphate (AsF sub.6 sup.-), benzene sulfonate ($\text{C sub.6 H sub.4 SO sub.2 sup.-}$), etc. Similarly, sulfonic anhydrides ($\text{R-SO sub.2 -O-SO sub.2 -R'}$) or carbonyl anhydrides (R-CO-O-CO-R') may be used as alkyl Lewis acids; in these formulas, R and R' may be the same (e.g., as in tosylic anhydride or 5-norbornene-2,3-dicarboxylic anhydride) or different.

Detailed Description Paragraph Right (3)

Exemplary Lewis acids which may be employed in accordance with the present invention

include the following: benzene sulfonyl chloride, p-toluene sulfonyl chloride, p-toluene sulfonic anhydride, trimethyl silyl chloride, benzyl bromide, 4-bromo-1-butene, chlorophenyl methyl ketone, 1,4-dichlorothionyl-benzene, dimethyl sulfate, methyl sulfate, methyl iodide, trimethyl oxonium tetrafluoroborate, p-toluenesulfonyltriflate, aluminum trichloride (AlCl_3), boron trichloride (BCl_3), copper chloride (CuCl_2), tungsten hexacarbonyl (W(CO)_6), etc. As this representative list illustrates, there is available an extremely broad range of suitable Lewis acids which may be employed in accordance with the inventive method. The selection of suitable dopant materials by those working in the field would be routine, as virtually any desired anion or cation may be provided in the form of a Lewis or Bronsted acid.

U.S. Reference US Cross Reference Classification (30):
210/500.38

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L3: Entry 1 of 3

File: USPT

Oct 6, 1992

DOCUMENT-IDENTIFIER: US 5152901 A

TITLE: Polyamine-polyamide composite nanofiltration membrane for water softening

Abstract Paragraph Left (1):

A thin film composite (TPC) ultrafilter/hypermfilter water softening membrane on a microporous substrate is produced by an interfacial polymerization reaction between (1) an aqueous phase comprising a blend of water soluble and water dispersible compounds, the former containing piperazine and polyamines, the latter using a chlorine or other oxidant reacting compound which protects the resulting membrane from damage by any chlorine present and (2) an organic phase comprising polyfunctional agents capable of reacting and/or polymerizing with one or more of the ingredients of said aqueous phase.

Brief Summary Paragraph Right (1):

This invention is directed to a composition of matter which allows the pressure membrane separation of calcium and magnesium salts from sodium salts in either chloride or preferably mixed chloride-sulfate form. The aforementioned composition of matter is a highly crosslinked polyamine-polyamide polymerized upon a microporous polysulfone sheet and co-blended with a latex polymer having the ability to react with chlorine or other oxidants while processing feed streams for the separation of calcium (or magnesium) from sodium salts. This composition of matter is a nanofiltration membrane which lies between hyperfiltration (rejects both calcium and sodium salts) and ultrafiltration (rejects neither calcium or sodium salts). This composition of matter is also a hypochlorite or chlorine resistant nanofiltration membrane capable of filtering out organic molecules having molecular weights generally exceeding 200 Daltons.

Brief Summary Paragraph Right (2):

Salt and solute rejecting membranes suitable for use in the desalination of aqueous solutions are the subject of numerous patents. Casotte (U.S. Pat. No. 4,259,193) discloses permselective (salt rejecting) multilayer membranes in which there is a microporous polysulfone substrate layer and a juxtaposed polyamide layer made from an aromatic triaryl-halide and an essentially monomeric, polyfunctional secondary amine. Scala et al (U.S. Pat. No. 3,744,642) discloses multilayer membranes in which one layer is a porous substrate and the other juxtaposed layer is a polyamide, a polyphenyl ester, or a polysulfonamide. Hara et al (U.S. Pat. No. 4,253,802) discloses semipermeable composite membranes in which the membrane material is crosslinked using polyfunctional aromatic acid halides. Kamiyama et al. (U.S. Pat. No. 4,619,767) discloses permselective multilayer membranes having (1) a microporous substrate layer (2) an ultra thin layer of a crosslinked polyvinyl alcohol/amino compound and (3) a porous inner layer of water insoluble polyvinyl alcohol located between the porous substrate and the ultrathin layer. Other patents disclosing the preparation and properties of thin film composite membranes are U.S. Pat. Nos. 3,951,815; 4,065,012; 4,039,440; 4,277,344; 4,885,091; 4,395,661; 4,802,984; 4,313,816 and many others.

Brief Summary Paragraph Right (3):

A discussion of chlorine tolerance of reverse osmosis membranes, (equally applicable to nanofiltration membranes be they anisotropic or thin film composite) is presented by Albert J. Petersen in a 1986 paper entitled "The Expanding Roster of Commercial Reverse Osmosis Membranes". It was stated therein that the thin film composite membranes in which the thin polyamide layer was composed of the reaction product of trimesoyl chloride and piperazine had the best chlorine tolerance for a polyamide TFC membrane, but might not be fully resistant to chlorine degradation despite these claims. Time has proven these claims of chlorine resistance to be invalid.

Brief Summary Paragraph Right (4):

A polymeric material having a large surplus of primary, secondary, and even tertiary amine functionalities will have a large chlorine tolerance to hypochlorine or chlorine containing solutions in the 0.1 to 1.0 ppm concentration range. The thin film composite membranes of the present invention have intentionally been constructed with large excesses of amine functional groups for the express purpose of upgrading their abilities to neutralize and tolerate small quantities of chlorine or hypochlorites which may be present in water to which these TFC membranes may be exposed. Simultaneously, the membranes of the present invention are also protected against chlorine destruction by the co-addition of double bond containing water miscible latexes. These become a mixed component of the TFC during the formation of the thin film polyamides at the interface of a hexane solution containing acyl chlorides and the aqueous phase containing piperazine, polyamines, a butadiene-styrene latex and caustic to accelerate the formation of the interfacial polyamides. The unsaturated latex (the subject of W. A. Waite's U.S. Pat. No. 4,912,815) reacts with chlorine present in feed waters to also render the TFC membrane chlorine tolerant.

Brief Summary Paragraph Right (5):

The nanofiltration membrane of the present invention will contain two species capable of making the TFC membrane chlorine (or hypochlorite) tolerant. These species are:

Brief Summary Paragraph Right (7):

b.) Polyamines incorporated into the TFC polyamide ##STF1##

Brief Summary Paragraph Right (8):

The addition of polyamides to the composition of the amino portion of the TFC polyamides of the present invention have been found to do much more than provide a reducing compound for the neutralization of excess chlorine normally added to the feed waters to be treated.

Brief Summary Paragraph Right (9):

The polyamines used in preparing the TFC polyamine-polyamide of this invention also provide excess crosslinking capability during the formation of the TFC polyamide. Thus excess crosslinkage, when reacted with diacyl or triacyl halides to form a polyamine-polyamide thin film has been found to effect the degree separation of sodium and alkaline earth salts such as Ca.sup.+2 and Mg.sup.+2 . One such example of a polyamine is tetraethylene pentamine (TEPA):

Brief Summary Paragraph Right (10):

The prior art has not addressed the end effect of creating a thin film composite reverse osmosis or nano-filtration membrane having chlorine tolerance and a very high degree of crosslinking during the formation of the thin film polyamides. A very high degree of crosslinking during interfacial polymerization will tend to give 1) a much lowered degree of polymer chain flexibility, (i.e. very high network structures) by the use of multifunctional amino compounds to react with the diacyl or triacyl halides and 2) a polymeric structure which will have great difficulty in close packing and forming crystalline bundles or zones via hydrogen bonding or Van Der Waal bond attractions. This high degree of crosslinking of the TFC polymerizate will yield a stiff, inflexible structure having defined pore sizes of small but inflexible diameters. As shown in the examples hereinafter, it appears that the pores are of such size as to exclude hydrated Ca.sup.+2 ions and Mg.sup.+2 ions in preference to hydrated Na.sup.+1 ions regardless of the anions associated with each. This results in a polymerizate that will remove hardness from feed waters under a pressure differential.

Brief Summary Paragraph Right (11):

The present application discloses how to effect variances in pore sizes of thin film composite polyamides by the incorporation of polyamines into a formulation containing piperazine followed by reaction with di and triacyl halides.

Brief Summary Paragraph Right (12):

It will also be shown how the incorporation of polyamines into the TFC formulation allows for a distinct separation (under low pressures) of calcium and magnesium salts from sodium salts thus yielding a pressure driven softening membrane.

Brief Summary Paragraph Right (14):

It will also be shown hereinafter that exhaustive methylation of the unreacted amino groups (whereby all electron pairs are covered by methyl groups) does not appear to affect the separation of calcium (or magnesium) salts from sodium salts. Both the rejection and flux rate of the TFC membranes were changed by methylation but not the degree of separation of bivalent cation from univalent cation. It does appear that

exhaustive methylation changed the pore sizes of the lightly crosslinked TFC. This would be expected whence methyl chloride groups are added to the TFC structures, and affected both Na.sup.+ as well as Ca.sup.+2 to the same degree of rejection hence no coordination of Ca.sup.+2 can be in force during the pressure driven separation of calcium salts from sodium salts. The noted increase in flux rate during the testing of the methylated vs. unmethylated TFC membranes is credited to a small degree on the pore size increase during methylation of the polyamine-polyamide network structure and is not surprising.

Brief Summary Paragraph Right (15):

It will further be shown, that in the absence of polyamines during the preparation of the thin film composite structure, that the simple polyamide structure gave nearly equivalent separations of sodium and calcium ions under pressure with both ions being removed at high rejection rates.

Brief Summary Paragraph Right (16):

In this try, this invention describes a synthetic route to the preparation of nanofiltration membranes which can easily separate at respectable flux rates, salts of sodium from those of calcium or magnesium whether in the chloride, sulfate or mixed chloride-sulfate form. One may also separate sucrose from sodium chloride at the same time. The membrane has chlorine tolerance and in principle is merely a copolymerization of triacyl or diacyl halides with a mixture of polyamine, latex polymers containing unsaturation and piperazine; the resulting network polyamide being spatially structured to separate alkali metal salts from alkaline earth metal salts.

Detailed Description Paragraph Right (1):

The procedures of W. A. Waite (U.S. Pat. No. 4,913,815) are illustrative of the conditions needed for preparing thin film composite membranes of the present invention. The process consists essentially of several steps as follows:

Detailed Description Paragraph Right (2):

A microporous substrate with pores in the range of 0.005 to 0.5 microns in diameter is prepared. This may be accomplished preferably with a polysulfone linear polymer, cast from a 15% solution thereof in dimethyl formamide solvent and immediately quenched in ultrapure water to precipitate the polysulfone membrane and extract its solvent.

Detailed Description Paragraph Right (3):

This base membrane substrate (dried and stored, or fresh and wet) is then equilibrated with a "water phase" solution containing the desired emulsion, amino compound, polyamine compound, etc.; and the excess solution removed from the surface by a draining, rolling, or sponging procedure. The concentration of the components in the "water phase" solution is an important factor in the performance of the resulting composite.

Detailed Description Paragraph Right (6):

It is normal practice to treat feed waters with small amounts of chlorine or sodium hypochlorite, so as to kill harmful microorganisms present in water. After chlorination it becomes necessary to remove any residual chlorine and other oxidants (in some cases even dissolved oxygen of the air) remaining in the feed water prior to reverse osmosis treatment since such oxidants are known to irreversibly damage the polyamide thin film of the membrane and substantially reduce their performance resulting in premature failure. Removal of residual chlorine in the feed water is accomplished both by reductive reaction with the polyamine-polyamide TFC of this invention and concurrently therewith by reaction with the reducing latex polymer co-precipitated with the TFC polyamine-polyamide thin film.

Detailed Description Paragraph Right (9):

A very large number of synthetic latices are available commercially and are readily blended into the thin film composite membranes of this invention. Such latices include, for example, nitrile latexes (aqueous, anionic dispersions of butadiene-acrylonitrile copolymer), styrene butadiene latexes, styrene-butadiene-4-vinyl pyridine latexes, phenolic latexes, resorcinol-formaldehyde latexes, and other latexes which will reduce chlorine, hypochlorite ion, hypochlorous acid, or other oxidants such as hydrogen peroxide, sodium carbonate peroxide complex, ozone, persulfates, bismuthates, or permanganates.

Detailed Description Paragraph Right (11):

One amino compound used in this invention is enumerated in Cadotte (U.S. Pat. No. 4,259,183) namely piperazine ##STR5## a secondary amine having two (N-H) groups so as

to react with a mixture of isophthaloyl chloride and/or trimesoyl chloride to form a thin polyamide in the presence of a second polyamine compound and a reducing double bond containing polymeric latex onto a microporous polysulfone sheet to form the membrane. The second polyamine which is a reducing amine and a principal component of this solution, is typified by the compound tetraethylene pentamine. This polyamine, copolymerized with piperazine, with the above acylchlorides (either as a mixture of the two acylchlorides or individually) forms a very highly crosslinked polyamine-polyamide film into a microporous polysulfone sheet.

Detailed Description Paragraph Right (19):

The composite semipermeable membrane is prepared according to the present invention by coating or impregnating a porous substrate with an aqueous solution comprising a water soluble or dispersible reducing latex, (one containing ##STR10## double bonds in the organic polymer latex structure or containing reducing organic chemical groups including primary amino, secondary amino (capable of forming imines [i.e. -C(=O)-NH-]), phenolic, catecholic, hydroquinonic, resorcinolic, or any other organic functional group, polymeric material or organic material, which are capable of being easily oxidized by chlorine or hypochlorites) and a combination of amino compounds one of which is a polyamine compound and the other an amino compound having at least two secondary amino groups in the molecule, thereafter contacting the porous substrate with a polyfunctional crosslinking reagent capable of reacting with secondary amino groups to polymerize the amino compounds by crosslinking, and then heating or drying to remove solvents and/or postcure the polyamine-polyamides.

Detailed Description Paragraph Right (20):

The porous substrate used in the present invention is suitably a membrane having an asymmetric structure wherein the surface pore size is generally from 50 to 500 μ ANG. For example, polysulfone, polyether sulfone, or polyvinylidene fluoride can preferably be used.

Detailed Description Paragraph Right (21):

Particularly, polysulfone is more desirous for preparation of this porous base film substrate because of its demonstrated oxidative stability. The porous membrane may be re-inforced by backing with a fabric or a non-woven web material.

Detailed Description Paragraph Right (24):

The acyl chloride (bromide or iodide) reagent used in the present invention is a compound having 2 or more functional groups (capable of reacting with primary and secondary polyamine compounds as well as with secondary di-amino compounds related to piperazine or any other organic functional group possessing a reactable proton such as the hydroxyl group, amide groups, mercaptan groups, or mixtures thereof, for example, one or more kinds of acid halide groups, halogen sulfonyl groups, N-halo formyl groups, haloformate groups and acid anhydride groups, etc. in the molecule. Preferred examples include isophthaloyl chloride, terephthaloyl chloride, trimellitic acid chloride, trimellitic anhydride chloride, benzene-1,3-disulfonyl chloride, phoslinic acid chloride, 5-chlorosulfonyl isophthaloyl chloride, and piperazine-N,N-dicarboxylic acid dichloride. Isophthaloyl chloride and trimesoyl chloride are particularly preferable. Other crosslinkers would include multifunctional isocyanates.

Detailed Description Paragraph Right (27):

It was then immersed for 30 seconds in the organic phase solution, that is, a n-hexane solution of 1% crosslinkers i.e. 0.4% by weight of trimesoyl chloride and 0.6% by weight of isophthaloyl chloride. The substrate was removed, allowed to dry in air and then allowed to set overnight at room temperature. The resulting thin film-latex impregnated composite membrane was tested in a stirred F.O. test cell at 60 psi using the following solutions consecutively.

Detailed Description Paragraph Right (28):

The above membrane which had no polyamine in its formulation, rejected both Ca^{+2} and Na^{+} nearly equivalent and thus is not a good softening membrane.

Detailed Description Paragraph Right (29):

Membranes were fabricated and tested as in Example 1 using the following mixture in 100 ml pure water:

Detailed Description Paragraph Right (30):

Membranes were fabricated and tested as in Example 1 using a membrane formulation based on 1% by weight of material in 100 ml of pure water as follows:

Detailed Description Paragraph Right (31):
Membranes were again fabricated and tested as in Example 1 using the following formulation:

Detailed Description Paragraph Right (33):
Membrane formulation is as follows:

Detailed Description Paragraph Right (35):
Membrane formulation is as follows:

Detailed Description Paragraph Right (37):
membrane formulation:

Detailed Description Paragraph Right (39):
The membrane of Example #8 was tested with Solution #2 adjusted to a pH of 8.80 by addition of 1.0N NaOH.

Detailed Description Paragraph Right (42):
The pH variance to $\text{Ca}_{\text{sup.}+2}$ separations in Examples 8 and 9 show that the nitrogen electron pairs on the excess unreacted polyamines of the TFC of this invention do not appear to affect the transport of $\text{Ca}_{\text{sup.}+2}$ ions across these membranes probably because of the $\text{Ca}_{\text{sup.}+2}$ ##STR1## coordination.

Detailed Description Paragraph Right (43):
The membrane of Example #7 was washed with 1N ammonium hydroxide for ten minutes and then immersed for 1 hour in methyl alcohol to remove water. It was noticed that the TFC layer which is normally the concave part of the 13/4" circle, switched to being the convex part due to the alcohol immersion. This membrane was then placed in a constantly saturated methyl alcohol solution of methyl chloride overnight (or 16-18 hours) so as to convert most free amino groups still present in the TFC membrane into quaternized ammonium halides. This procedure removes available electron pairs from each amino nitrogen and is a test to see whether calcium ##STR1## coordination possibilities can be removed from this membrane as an attempt to determine if nitrogen-calcium complexes are the reasons why calcium is being selectively detained from passage through the membrane. Sodium ions do not coordinate with the electron pairs of polyamino compounds.

Detailed Description Paragraph Right (44):
After overnight reaction the membrane is immersed in water whence the convex TFC (non methylated) switched back to concave part. The membrane was mounted in a stirred R.C. test cell and tested as follows:

Detailed Description Paragraph Right (45):
The results show that the exhaustive methylation of the Example #7 membrane caused both the rejections of calcium and sodium to drop and the flux to essentially double. This is indicative of pore size amplification and apparently dispels any mechanism whereby $\text{Ca}_{\text{sup.}+2}$ is being coordinated by unquaternized amino nitrogens at a pH of about 8.7.

Detailed Description Paragraph Right (46):
The membrane of Example #10 (i.e. methylated membrane from Example #7) was tested once again using solution #2 which had its pH raised by addition of 8N KOH.

Detailed Description Paragraph Right (47):
The results of Examples 10 and 11 show that the exhaustive methylation of the membrane of Example #7 gives $\text{Ca}_{\text{sup.}+2}$ and $\text{Na}_{\text{sup.}+}$ rejections of similar magnitudes regardless of the solution pH. Flux is increased to 14.3 from 11.7 which is believed not significant in comparison to the twofold flux increase due to methylation.

Detailed Description Paragraph Right (48):
Again it has been shown that decreasing the availability of the nitrogen electron pairs (i.e. by acidification or methylation) does not affect the transport across membranes of calcium ions due to coordination complex formation.

Detailed Description Paragraph Right (49):
The membrane of Example 5 was tested with a Solution #3, a high solids water (about 3200 ppm) containing about 2000 ppm hardness as CaCO_3 and a sulfate to chloride ratio of nearly 4 to 1. Sodium ions were present in approximate concentrations of about 200 ppm while calcium and magnesium came to a combined total of 685 ppm.

Detailed Description Paragraph Right (51):

A membrane emulsion using no latex was prepared as follows:

Detailed Description Paragraph Right (52):

The results show that the membrane (without a latex of polystyrene-butadiene in the aqueous phase) failed in separating calcium salts from sodium salts and thus is not classified as a nanofilter softening membrane.

Detailed Description Paragraph Right (53):

A similar membrane was prepared as in Example #1 except that no latex was included, thus this membrane did not contain any latex or polyamine.

Detailed Description Paragraph Right (55):

The membrane of Example 6 was pressure tested at 60 psi using a solution mixture of 500 ppm sucrose (MW=342.3 Daltons) and 200 ppm Ca.sup.+2 (680 ppm CaSO.sub.4) and evaluated for salt-sugar separation. The following was found:

Detailed Description Paragraph Right (57):

The membrane of Example 6 was tested in a solution of 500 ppm dextrose (MW=180.2 Daltons) and 200 ppm Ca.sup.+2 (680 ppm CaSO.sub.4) at 60 psi and evaluated for salt-dextrose separation.

Detailed Description Paragraph Right (60):

The membranes from Examples 1, 2, 5, 13 and 14 were concurrently tested (at 25 degree C) over a 32 day period for chlorine tolerance and for rejection and water flux in treating a mixed 200 ppm Ca.sup.+ (680 ppm CaSO.sub.4)-150 ppm Na.sup.+ (281.5 ppm NaCl) solution at a pH of 3.8-4.0 in the presence of 200 ppm (maintained) chlorine (a total exposure of 150,000 ppm-hrs of chlorine).

Detailed Description Paragraph Right (61):

The test results show (based on % rejection) that membranes prepared with the polyamine TEPA have improved resistance to hypochlorite oxidation even where the latex emulsion is not an added ingredient as is the case in the membrane of Example 13. It appears that the polyamine is preferentially oxidized over that of the polyamide piperazine.

Detailed Description Paragraph Left (1):

where P=0,1,2,3, etc. along with piperazine, to interfacially polymerize with any polyfunctional acyl halide so as to form a highly crosslinked film of polyamine-polyamide interfacially.

Detailed Description Paragraph Left (10):

The results show that excess polyamine (TEPA) in reaction with tri and diacyl halides does not appear to produce a desirable softening membrane.

Detailed Description Paragraph Left (12):

The results show an about 2:1 piperazine to polyamine weight content gives a fair softening membrane in solution #2 (a mixture of calcium sulfate and sodium chloride) but not in mixed solution #1 (salts of calcium chloride and sodium chloride).

Detailed Description Paragraph Table (2):

	% Rejection Ca.sup.+2	% Rejection Na.sup.+	Flux
GFD*	53.2	60.0	12.2
88.4 9.7			
membrane per day.			

*Gallons of solution per square foot of

Detailed Description Paragraph Table (24):

INITIAL TEST	32 DAY TEST	MEMBRANE	TEPA/	EMULSION	% CA sup.+2	% NA sup.+2	FLUX	%	RATIO
CA sup.+2	FLUX	EXAMPLE	PIPERAZINE	USED	REJECTION	REJECTION	REJECTION	REJECTION	(GFD) %
07.25	= 0	POLYSTYRENE-	95.1	9.7	88.4	16.3	48	0	8
PS-BUTADIENE	44.0	13.0	5.9	8.2	101.6	0	6	.04	.21
45.9	3.2	13	08/.42	= 0.190	NONE	95.2	4.8	95	4
18.0	76.4	0	61.6	0					

(PS) BUTADIENE 2 .02/.23 = 0.087
 190 PS-BUTADIENE 94.4 1 24.5 22.4
 NONE 57.1

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L29: Entry 1 of 4

File: USPT

Jan 8, 2002

DOCUMENT-IDENTIFIER: US 6337018 B1
TITLE: Composite membrane and method for making the same

Abstract Paragraph Left (1):

A composite membrane and method for making the same, comprising a porous support and a crosslinked polyamide surface. The subject membrane provides improved flux and/or rejection rates. The subject membrane is further capable of operating at lower operating pressures. The subject method includes reacting a polyfunctional amine with a polyfunctional acyl halide to form a polyamide. The method includes the step of contacting a phosphorous containing compound with the polyfunctional acyl halide prior to and/or during the reaction between the polyfunctional acyl halide and a polyfunctional amine. The subject process is easily adapted to commercial scale manufacturing processes and is particularly suited for making nanofiltration and reverse osmosis composite membranes.

Brief Summary Paragraph Right (5):

Among particularly useful membranes for reverse osmosis and nanofiltration applications are those in which the discriminating layer is a polyamide. The polyamide discriminating layer for reverse osmosis membranes is often obtained by an interfacial polycondensation reaction between a polyfunctional amine and a polyfunctional acyl halide as described in, for example, U.S. Pat. No. 4,277,344, which is incorporated herein by reference. In contrast to reverse osmosis membranes, the polyamide discriminating layer for nanofiltration membranes is typically obtained via an interfacial polymerization between a piperazine or an amine substituted piperidine or cyclohexane and a polyfunctional acyl halide as described in U.S. Pat. Nos. 4,769,148 and 4,859,384. Another way of obtaining polyamide discriminating layers suitable for nanofiltration is via the methods described in, for example, U.S. Pat. Nos. 4,769,897; 4,812,270; and 4,824,574. These patents describe changing a reverse osmosis membrane, such as those of U.S. Pat. No. 4,277,344, into a nanofiltration membrane.

Brief Summary Paragraph Right (6):

Composite polyamide membranes are typically prepared by coating a porous support with a polyfunctional amine, most commonly coated from an aqueous solution. Although aqueous solutions are preferred, non-aqueous solutions may be utilized, such as acetyl nitrate and dimethylformamide (DMF). A polyfunctional acyl halide is subsequently coated on the support, typically from an organic solution. Although no specific order of addition is necessarily required, the aqueous amine solution is typically first coated on the porous support followed by the organic acyl halide solution. Although one or both of the polyfunctional amine and acyl halide may be applied to the porous support from a solution, they may alternatively be applied by other means such as by vapor deposition.

Brief Summary Paragraph Right (8):

Methods of improving membrane performance by post-treatment are also known. For example, U.S. Pat. No. 5,876,602 to Jons et al. describes treating a polyamide composite membrane with an aqueous chlorinating agent to improve flux, lower salt passage, and/or increase membrane stability to base. U.S. Pat. No. 5,755,964 to Mickels discloses a process wherein the polyamide discriminating layer is treated with ammonia or selected amines, e.g., butylamine, cyclohexylamine, and 1,6 hexane diamine. U.S. Pat. No. 4,765,897 to Cadotte discloses the post treatment of a membrane with a strong mineral acid followed by treatment with a rejection enhancing agent. U.S. Pat. Nos. 4,765,897; 5,876,602 and 5,755,964 are incorporated herein by reference.

Brief Summary Paragraph Right (10):

The present invention provides an improved composite membrane and method for making the

Brief Summary Paragraph Eight (14):

Brief Summary Paragraph Right (15):

Exer. Summary Paragraph Eight (20):

Brief Summary Paragraph Right (21):

6:50:29 32 PM

the polyamide in the same solvent. The polyamide may then be isolated and pressed into a 13 mm diameter disk using a die and an hydraulic press (10,000 lbs. load). The resulting disk may be placed between two layers of polypropylene sample support film (0.1 micron thickness) and attached to a Chemplex 30 mm diameter XRF sample cup using a stainless support ring. The sample can be measured in a plastic insert with a Pb mask. Measurements can be obtained on both sides of the disk and averaged together. Once prepared, the sample can be analyzed with a Philips PW1480 wavelength dispersive X-ray fluorescence spectrometer equipped with a scandium anode 3 KW X-ray tube. For measurement of Phosphorous, K alpha X-ray intensity the instrument can be operated under the following conditions: 50 kV, 50 mA, germanium crystal (2 θ =6.63 $^\circ$ angstroms), gas flow proportional detector (argon/methane), upper and lower discriminator level 80/25, He purge. The Phosphorous K alpha peak can be measured at a 2 theta angle of 141.035 and backgrounds can be measured at + and - offsets of 1.5. Peak and background measurements are commonly taken for 10 seconds each.

Brief Summary Paragraph Eight (20):

In preferred embodiments, the subject polyamide composite membrane includes at least about 1 microgram (and more preferably at least 5 micrograms, even more preferably 15 micrograms and in some embodiments at least 30 micrograms) of "retained" phosphorous per gram of polyamide. As indicated, the retained phosphorous is believed to be a result of the formation of a complex between the phosphorous containing compound and the acyl halide. Although dependent upon the relative density of the polyamide layer, most membranes of the subject invention will include at least 0.02 micrograms of phosphorous per square meter of membrane, but more commonly more than about 1 microgram of phosphorous per square meter of membrane.

Brief Summary Paragraph Eight (23):

The phosphorous containing compounds of the present invention are not particularly limited and different species of compounds may be used in combination. However, preferred species are non-pyrophoric, sufficiently stable in air and water (i.e., the species do not decompose, degrade or significantly react with water or air within the time period of the subject method), and have suitable industrial hygiene properties, e.g., do not pose significant environmental hazards, do not require expensive handling requirements, do not pose significant safety concerns, etc. The subject phosphorous containing compounds are preferably "substantially soluble" in the organic solutions as described herein. The term "substantially soluble" is intended to mean that a sufficient quantity of the phosphorous containing compound dissolves in the solution to result in a final membrane having improved flux, rejection and/or lower operating pressure as compared to an identical membrane prepared without the subject phosphorous containing compound. An additional indicia that the phosphorous containing compound is "substantially soluble" is the presence of a detectable quantity of retained phosphorous in the polyamide layer. When used at effective concentrations the subject phosphorous containing compounds preferably dissolve and form a single homogeneous phase within the organic solutions previously described. Preferred phosphorous containing compounds have a solubility parameter of from about 15 to about 20, and more preferably from 14 to 23 J.sup.1/2 cm.sup.3/2.

Brief Summary Paragraph Eight (49):

A variety of membrane shapes are commercially available and useful in the present invention. These include spiral wound, hollow fiber, tubular, or flat sheet type membranes. In regard to the composition of the membrane, often the discriminating layer has hygroscopic polymers other than the polyamide coated upon the surface of the discriminating layer. Among these polymers are anionic, cationic, neutral and zwitterionic such as polymeric surfactants, polyvinyl alcohol, polyethylene imine and polyacrylic acid.

Brief Summary Paragraph Eight (51):

For example, as described in U.S. Pat. No. 5,875,602, membrane stability to strong base exposure while maintaining flux and salt passage can be achieved by contacting the membrane, after it has been formed on a porous support, whether in flat sheet or element form, with a hypochlorite solution at a pH of at least 10.5. The optimal exposure time depends on the temperature and concentration of the hypochlorite used. At room temperature, conditions which achieve the stated goals can generally be found within the ranges of 15 minutes to 5 hours and at concentrations of 200 to 10,000 ppm by weight of hypochlorite, measured as chlorine. Preferred concentrations of hypochlorite are 500 to 7,000 ppm; preferred exposure times are 30 minutes to three hours. In a preferred embodiment the membrane is subjected to a heat treatment before being exposed to the aforementioned chlorine treatment. The membranes are heated in water at a temperature of 40 degree. C. to 100 degree. C. for times of 30 seconds to 24

Brief Summary Paragraph Right (53) -

Brief Summary Paragraph Eight (55:1)

Brief Summary Paragraph Right (56):

Brief Summary Paragraph Right (57):

Brief Summary Paragraph Eight (59):
The following terms

6:50:29.32 PM

the membrane. "Reverse osmosis membrane" is a membrane which has a rejection rate for NaCl of from about 95 to about 100 percent. "Nanofiltration membrane" is a membrane which has a rejection rate for NaCl of from about 90 to about 95 percent and has a rejection rate for at least one divalent ion or organic compound of from about 20 to about 100 percent. "Polyamide" is a polymer in which amide linkages $-CO-NH-$ occur along the molecular chain.

Issued US Original Classification (1):
210/500.38

Current US Original Classification (1):
210/500.38

Field of Search Class/SubClass (2):
210/500.38

U.S. Reference US Original Classification (15):
210/500.38

U.S. Reference US Original Classification (16):
210/500.38

U.S. Reference US Original Classification (17):
210/500.38

CLAIMS

1. A method for making a composite membrane comprising the non-sequential steps of coating a porous support with: (i) a solution containing a polyfunctional amine and (ii) a solution containing a polyfunctional acyl halide, wherein the polyfunctional amine and polyfunctional acyl halide are contacted with each other and react to form a polyamide layer on the porous support, the process being characterized by the step of contacting a phosphorous containing compound with the polyfunctional acyl halide prior to the reaction between the polyfunctional acyl halide and polyfunctional amine wherein the phosphorous containing compound has a solubility parameter of from about 15 to about 26 J.sup.1/2 cm.sup.3/2.
6. The method of claim 1 wherein the phosphorous containing compound is reacted with the polyfunctional acyl halide prior to and/or during the step of contacting the polyfunctional amine and polyfunctional acyl halide such that the resulting polyamide layer comprises a detectable quantity of retained phosphorous.
25. The method of claim 1 wherein the polyamide layer is contacted with a solution containing from 200 to 10,000 ppm of hypochlorite ion at a pH of at least 10.5.
26. The method of claim 25 wherein the polyamide layer is heat treated by contact with water at a temperature of 40 degree. C. to 100 degree. C. before contacting the membrane solution with the containing hypochlorite ion.
27. The method of claim 1 wherein the polyamide layer is contacted with an amine selected from the groups consisting of ammonia, substituted ammonia, butylamine, cyclohexylamine, and 1,6 hexane diamine.
28. The method of claim 1 wherein the polyamide layer is contacted with a strong mineral acid.
30. A method for making a composite membrane comprising the steps of coating a porous support with an aqueous solution containing a polyfunctional amine followed by subsequently coating an organic solution containing a polyfunctional acyl ##STR7## halide such that the polyfunctional amine and polyfunctional acyl halide are contacted with each other and react to form a polyamide layer on the porous support, the process being characterized by the step of including from 0.001 to 10 weight volume percent of a non-pyrophoric phosphorous containing compound within the polyfunctional acyl halide solution, wherein the phosphorous containing compound has a solubility parameter of from about 15 to about 26 J sup.1/2 cm.sup.3/2, an energy of interaction with the polyfunctional acyl halide of greater than 4.0 kcal/Mole and is represented by the formula:

6:50:29.32 PM

TITLE: Chlorine-resistant semipermeable membranes

DATE ISSUED: May 14, 1989

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Tran; Chinh N.	San Diego	CA		
Chu; Hong C.	San Diego	CA		
Light; William G.	San Diego	CA		

US-CL-CURRENT: 427/245; 210/500.33, 210/500.37, 210/500.38, 210/500.41, 427,341,
428/420

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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☐ 4. Document ID: US 4812238 A

L29: Entry 4 of 4

File USPT

Mar 14, 1989

US-PAT-NO: 4812238

DOCUMENT-IDENTIFIER: US 4812238 A

TITLE: Membranes prepared via reaction of diazonium compounds or precursors

DATE-ISSUED: March 14, 1989

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cadotte; John E.	Minnetonka	MN		
Schmidt; Donald L.	Midland	MI		

US-CL-CURRENT: 210/636; 210/500.3, 210/500.37, 210/500.38, 210/655

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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